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NONAROMATIC ISOXAZOLINEDIAZONIUM SALTS

V. I. Rybinov, M. V. Gorelik, M. Ya. Mustafina, and V. Ya. Gurvich

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Diazotization of 3-aminoisoxazolines has given stable, nonaromatic 2-isoxazoline-3-diazonium salts which undergo the azo-coupling reaction. The electronic structures of these diazo- and azo-compounds are discussed.

Direct diazotization of the appropriate amines in aqueous media has given the nonaromatic 2-pyrazoline-3-diazonium [1, 2] and 1,3,4-thiadiazoline-5-diazonium salts [3] (the reactivity of which is comparable with that of aromatic salts). Continuing these investigations, we have examined the possibility of obtaining 2-isoxazoline-3-diazonium salts by diazotizing 3-amino-2-isoxazolines.

Treatment of the 3-amino-2-isoxazolines (I) with sodium nitrite in acetic, hydrochloric, phosphoric, or nitrosylsulfuric acid in acetic acid gives the 2-isoxazoline-3-diazonium salts (II), which are intermediate in terms of stability in aqueous solution between pyrazoline- and thiadiazolinediazonium salts. Pyrazolinediazonium salts are stable in aqueous hydrochloric acid at 20-25°C for several days [2], and thiadiazolinediazonium salts for a few seconds [3], while the cations (II) decompose under these conditions within 2-3 h.

5-Phenylisoxazolinediazonium fluoroborate (IIb) can be isolated in the solid state but, since it is less stable than pyrazolinediazonium salts, not in an analytically pure state. Its IR spectrum shows stretching vibrations for the diazonium group at 2280 cm^{-1}, i.e., in the range usual for aromatic diazonium salts (2290 cm^{-1} for benzenediazonium chloride [4]). In the case of pyrazolinediazonium cations, diazonium group absorption is seen, depending on the substituent X attached to $N_{(1)}$, between 2125 cm^{-1} when X = Ph and 2265 cm^{-1} when X = $PhSO_2$ [2]. It is therefore apparent that the tendency of the lone pair on oxygen in the isoxazolinediazonium cation (IIb) to conjugate with the C=N double bond and the diazonium group is less than that of the nitrogen in the 1-phenylpyrazolinediazonium cation, which is in accordance with a decreased contribution of the diazo-structure (II') as compared with its contribution in its pyrazoline analog.

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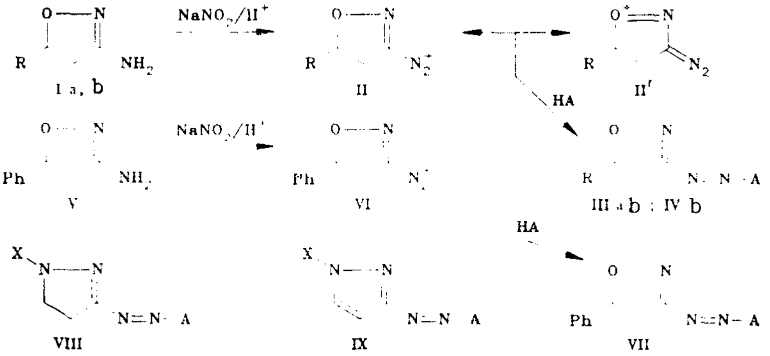

a R=H, b R=Ph; III, VII—IX A=4-Me$_2$NC$_6$H$_4$, IV A=4-MeOC$_6$H$_4$

The isoxazolinediazonium cations (II), like pyrazoline- and thiadiazolinediazonium cations, undergo the azo-coupling reaction. The decreased contribution of the diazo-structure (II') in the case of isoxazolinediazonium cations should result in an increase in their N-electrophilicity. In practice, the reactivity of the isoxazolinediazonium salts (II) in the azo-coupling reaction is so great that they give azo-compounds not only with N,N-dimethylaniline (III), but also with the relatively unreactive anisole (IV), the yield of (IVb) being around 70%, whereas the 1-phenylpyrazolinediazonium cation fails to react under these conditions. The aromatic 5-phenylisoxazole-3-diazonium cation (VI), obtained by diazotizing the aminoisoxazole (V), also fails to undergo azo coupling with anisole.

The PMR spectrum of (IIa) shows two triplets with a splitting constant of 5 Hz, typical of two adjacent methylene groups, at 3.18 (4-H) and 4.58 ppm (5-H). When a phenyl group is present in the 5-position of the isoxazoline ring, the degeneracy of the protons in the 4-position is removed, with the result that the PMR spectra of (IIIb) and (IVb) are characteristic AA'B systems, in which the signals for the equatorial and axial protons can be distinguished.

The long-wavelength absorption maximum in the electronic spectrum of the 3-arylazoisoxazolines (IIIa, b) is shifted hypsochromically relative to the absorption maximum for 3-arylazo-1-phenylpyrazoline (VIII, X = Ph) by 62-67 nm. According to quantum chemical calculations [5], the long-wavelength band of azo-compounds which do not contain strong π-electron acceptor substituents (such as NO$_2$) is due to the transfer of electron density to the azo-group. The greater electron donor capacity of the PhN$_{(1)}$ group in the pyrazoline (VIII) as compared with the oxygen in the isoxazolines (IIIa, b) facilitates the transfer of electron density from the heterocyclic fragment to the azo-group, resulting in longer-wavelength absorption. Confirmation that the increased donor nature of the heteroatom results in a deepening of the color of azo-compounds is provided by a comparison of the long-wavelength maxima of 1-X-3-arylpyrazolines when X is varied (509 nm for Ph and 473 nm for Ac [2]). Aromatization involving the lone pair on the heteroatom in the aromatic sextet on passing from the azo-compounds (III) and (VIII) to the azo-compounds (VII) and (IX) results in a convergence of the electron-donor ability of the heterocycles, with the result that the differences in the colors of the azo-compounds of isoxazoles and pyrazoles diminish (λ_{max} 440 and 434 nm, respectively). As a result, the hypsochromic shift on aromatization of the arylisoxazoline (VIII) and the arylpyrazoline (IX) amounts to 75 nm, and of the arylisoxazoline (IIIb) to the arylisoxazole (VII), only 7 nm.

Hence, the synthesis of stable nonaromatic 2-isoxazolinediazonium salts has confirmed the hypothesis, put forward on the basis of experimental data [2] and quantum chemical calculations [6], that the influence of the nature of the heteroatom Y in the chain Y–C=N–C–N$_2^+$ on the thermodynamic stability of five-membered heterocyclic diazonium salts is not of prime important. Replacement of nitrogen by the more electronegative oxygen on passing from the pyrazolinediazonium cation to the isoxazolinediazonium cation results in an increase in the N-electrophilicity of the latter, and intensification of the color of the 3-arylazoisoxazolines derived therefrom by azo-coupling, as compared with 3-arylazopyrazoles.

EXPERIMENTAL

Electronic spectra were obtained on a Specord M-40 spectrophotometer, in ethanol. PMR spectra were measured on a Bruker WP-80 CW (80 MHz) in CDCl$_3$, internal standard HMDS. Mass spectra were obtained on an LKB-9000 instrument.

The elemental analyses of (IIIa), (IIIb), (IVb), and (VII) for C, H, and N, and their M values, corresponded to the formulas given.

The 3-amino-2-isoxazolines (I) were obtained by standard methods, by reacting hydroxyurea with α,β-unsaturated nitriles in the presence of sodium methoxide in methanol [8].

3-(4-Dimethylaminophenylazo)-2-isoxazolines (IIIa, b). To a solution of 5 mmoles of the amine (Ia or Ib) in 10 ml of acetic acid at 15°C was added 5 ml of a 1 N solution (5 mmoles) of nitrosylsulfuric acid, and the mixture stirred for 1 h. N,N-Dimethylaniline (0.6 ml, 5 mmoles) was then added, and the mixture poured onto ice. The solid azo-compound which separated was filtered off and crystallized from ethanol.

3-(4-Dimethylaminophenylazo)-2-isoxazoline (IIIa). Yield 73%, mp 204-204.5°C. UV spectrum, λ_{max} (log ε): 442 nm (4.5). PMR spectrum: 3.02 (6H, s, NCH_3); 3.18 (2H, t, J = 5 Hz, CH_2C); 4.58 (2H, t, J = 5 Hz, CH_2O); 6.66-7.92 ppm ($4H_{arom}$).

3-(4-Dimethylaminophenylazo)-5-phenyl-2-isoxazoline (IIIb). Yield 69%, mp 181-182°C. UV spectrum, λ_{max} (log ε): 447 nm (4.6. PMR spectrum: 3.02 (6H, s, NCH_3); 3.25 (1H, m, CHC_{eq}); 3.65 (1H, m, CHC_{ax}); 5.84 (1H, m, CHO); 6.70-7.92 (9H, m, arom).

3-(4-Dimethylaminophenylazo)-5-phenylisoxaxole (VII) was obtained similarly. Yield 87%, mp 178-179°C. UV spectrum, λ_{max} (log ε): 440 nm (4.5). PMR spectrum: 3.10 (6H, s, NCH_3); 6.89 (1H, s, CHC); 6.75-8.05 ppm (9H, m, arom.).

3-(4-Methoxyphenylazo)-5-phenyl-2-isoxazoline (IVb). To a solution of 1.47 g (5 mmoles) of the amine (Ib) in 10 ml of 85% phosphoric acid at 0°C was added 0.70 g (5 mmoles) of sodium nitrite. After 1 h, a solution of 0.54 g (5 mmoles) of anisole in 10 ml of acetic acid was added, and the mixture stirred for 18 h at 25°C, whereupon the azo-compounds (IVb) separated. Yield 0.98 g (70%), mp 109.5-110°C (from aqueous DMF). UV spectrum, λ_{max} (log ε): 360 nm (4.6). PMR spectrum: 3.25 (1H, m, CH_{eq}); 3.80 (3H, s, CH_3O); 3.70 (1H, m, CH_{ax}); 5.85 (1H, m, CHO); 7.00-7.90 ppm (9H, m, arom.).

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